ART 34 AMDT

Claims

1. A liquid crystal compound of general formula (I)

$$(R^1)_n$$
 $(R^3)_p$ $(R^4)_q$

(I)

where X is O, S or Se,

each R^1 and R^3 are independently selected from cyano, halo, optionally substituted hydrocarbyl, optionally substituted alkoxy, optionally substituted heterocyclyl, a group $R^{13}C(O)O$ - where R^{13} is optionally substituted hydrocarbyl or carboxy or a hydrocarbyl ester or amide thereof, provided that at least one or group R^1 or R^3 is other than cyano or halo,

each R² and R⁴ is independently selected from halo, nitro, lower alkyl optionally substituted by halo, or a group R¹⁴C(O)O- where R¹⁴ is optionally substituted hydrocarbyl,

n is 1 or 2, m is 0, 1, 2 or 3, p is 1 or 2 and q is 0 or 1, provided n + m does not exceed 4 and p + q does not exceed 2, and further provided the compounds are other than a compound of formula (A) or (B)

$$R^{12}$$
 A' Z''' A'' Z'''' A'' A''

where R¹¹ is a C₁₋₈ alkyl group;

 R^{12} is H, or a C_{1-12} alkyl or C_{2-12} alkenyl group, either of which may be optionally substituted by one CN or CF₃ group or one or more halogen atoms; and wherein one or more $-CH_2$ -groups in the alkyl or alkenyl groups is optionally replaced by $-O_{-1}$ -S-,

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-C(O)-, C(O)O-, -OC(O)- or -OC(O)O- provided that oxygen and sulphur atoms are not directly linked to each other;

A' and A'' are indepedently selected from:

- a) a trans-1,4-cyclohexylene residue in which one or more non-adjacent CH2 groups can be replaced by -O- and/or -S-;
- b) a 1,4-cyclohexenyl residue;
- c) a 1,4-phenylene residue in which one or two CH groups can be replaced by N;
- d) a residue from the group 1,4-bicyclo(2,2,2)-octylene, piperidine-1,4-diyl, naphthalene-2,6-diyl, decahydronaphthalene-2,6-diyl and 1,2,3,4-tetrahydronaphtahlene-2,6-diyl;

whereby residues a), b) and c) can be substituted by CN, Cl, or F,

Z'' and Z''' independently represent -C(O)O-, -OC(O)-, -CH₂O-, -OCH₂-, -CH₂CH₂-, -CH=CH-, -C≡C- or a single bond and

g is 0,1 or 2

$$Z'-Y'-Ar-Y'-M$$
 $Z'-Y'-M$
 $Z'-Y'-M$
 $Z'-Y'-M$
 $Z'-Y'-M$

(B)

where

each Ar is a bond or a spacer group such as a C2-30 alkylene or C2-30 alkenylene group, optionally substituted with C1-4alkyl, fluoro, chloro, bromo, cyano, or hydroxy, and optionally interposed with one or more -O-, -S-, -NH-, -NR^c-, -COO-, OCO, OCOO or CO;

each M is independently selected from optionally substituted aliphatic, aromatic, heteroaliphatic or a heteroaromatic ring system,

X' is O, S, COO, OCOO, CONH or CONR° where R° is C₁₋₄alkyl; e and f are independently selected from 0,1 or 2, each Y' group is independently selected from O, S, COO, OCO, OCOO, CONH, NHCO, CONR^c, or NR^cCO where R^c is as defined above:

each Z' group is independently selected from hydrogen, cyano or a polymerisable group;

and further provided that the compound is other than a compound of formula

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$$H_{11}C_{8}$$
 $C_{11}H_{23}$
 $C_{11}H_{23}$

- 2. A compound according to claim 1 wherein n is 1, and m is 0 or 1.
- 3. A compound according to claim 1 or claim 2 wherein no more than one of the groups R^1 and R^2 is fluoro.

A compound according to any one of the preceding claims where one of R¹ or R³ is cyano or halo and the other is optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted alkenyl, optionally substituted alkynyl, an optionally substituted aryl, optionally substituted heterocyclyl, carboxy or an ester thereof.

A compound according to any one of the preceding claims wherein R¹ or R³ where these are other than cyano or halo are selected from groups of formula (i), (ii), (iii), (iv), (v), (vii) or (viii)

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$$R^{10} \longrightarrow R^{10} - (O)_x \longrightarrow (F)_z \qquad (ii)$$

$$R^{10} - (O)_x \longrightarrow (F)_y \qquad (F)_z \qquad (iv)$$

$$R^{10} - (O)_x \longrightarrow (F)_y \qquad (iv)$$

$$R^{10} - (O)_x \longrightarrow (F)_y \qquad (iv)$$

where x is 0 or 1, R^{10} is an C_{1-20} alkyl group, and y and z are independently selected from 0, 1 or 2.

. (viii)

(F),

6. A liquid crystal compound according to claim 1 which is of general formula (IA)

R10

(vii)

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where X is oxygen, sulphur or selenium, R^{1a} and R^{1b} are independently selected from hydrogen, cyano, halo, optionally substituted hydrocarbyl, optionally substituted heterocyclyl or carboxy or a hydrocarbyl ester or amide thereof, provided that at least one group R^{1a} or R^{1b} is other than hydrogen;

one of R^{17} or R^{18} is cyano, halo, optionally substituted hydrocarbyl, optionally substituted heterocyclyl or carboxy or a hydrocarbyl ester or amide thereof, and the other is hydrogen, halo, nitro, lower alkyl optionally substituted by halo, or a group $R^{15}C(O)O$ - where R^{15} is an optionally substituted hydrocarbyl group;

 R^{2a} and R^{2b} are independently selected from hydrogen, halo, nitro, lower alkyl optionally substituted by halo, or a group $R^{14}C(0)O$ - where R^{14} is as defined above; subject to the provisos that:

- (i) at least one group R^{1a} or R^{1b} or R¹⁷ or R¹⁸ is other than cyano or halo;
- (ii) where X is S, R^{17} is carboxy or a hydrocarbyle ster or amide thereof, R^{18} is hydrogen, R^{2a} and R^{2b} are not both fluoro;
- (iii) where X is O, R^1 is an optionally substituted hydrocarbyl or carboxy or a hydrocarbyl ester or amide thereof, R^{2a} is hydrogen, and R^{1b} and R^{2b} are both fluorine, then R^{17} is other than C_{1-8} alkyl.
- 7. A compound according to claim 6 wherein one of R^{1b} or R^{1a} or R¹⁷ or R¹⁸ in formula (IA) is cyano or halo and at least one of the said groups on the other ring of the bicyclic ring of formula (IA) is optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted alkenyl, optionally substituted alkynyl, an optionally substituted aryl, optionally substituted heterocyclyl, carboxy or a hydrocarbyl ester thereof.
- 8. A compound according to claim 1 of formula (II)

wherein R⁵ is a group R³ as defined above in claim 1, one of R⁷ and R⁸ is a group R¹ as defined in claim 1 and the other is hydrogen or a group R¹ as defined in claim 1; R⁶ is hydrogen, cyano or fluoro, Provided that where R⁵ is cyano or fluoro, at least one of R⁷ or R⁸ is optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted alkoxy, optionally substituted aryl, optionally substituted heterocyclyl, carboxy or an ester thereof; and where one of R⁷ or R⁸ is cyano or fluoro and the other is hydrogen, R⁵ is optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted alkoxy, optionally substituted alkoxy, optionally substituted aryl, optionally substituted heterocyclyl, carboxy or an ester thereof.

9. A compound according to claim 8 of formula (IIA)

$$R^{r}$$
 R^{g}
(IIA)

where R⁵ is cyano or fluoro, preferably fluoro, one of R⁷ and R⁸ is hydrogen and the other is an optionally substituted hydrocarbyl group or a heterocyclic group as described above.

A compound according to claim 9 wherein at least one of R⁷ or R⁸ is a group of sub-formula (i), (ii), (iii), (vi) or (viii) as defined in claim 5.

- A liquid crystal compound according to any one of claims 1 to 7 where X is oxygen.
 - 12. A liquid crystal compound according to claim 8 which comprises a compound of formula (II) where R⁶ is hydrogen or fluoro, and R⁹ is hydrogen or fluoro.

A liquid crystal mixture comprising a compound according to any one of the preceding claims.

14. A liquid crystal mixture according to claim 13 which comprises at least two different compounds according to any one of claims 1 to 12.

15. A liquid crystal device such as a liquid crystal display device (LCD) comprising a compound according to any one of claims 1 to 12 or a mixture according to claim 13 or claim 14.

- A liquid crystal compound according to any one of claims 1 to 12 or a mixture according to claim 13 or claim 14, which has electroclinic properties.
- An electroclinic device comprising a liquid crystal compound or a mixture according to claim 16.
- A liquid crystal compound according to any one of claims 1 to 12 or a mixture according to claim 13 or claim 14, which has cholesteric properties.
 - 19. A device comprising a liquid crystal compound or a mixture according to claim 18, wherein said device is a thermoptic, thermographic or electro-optical device.
- A liquid crystal compound according to any one of claims 1 to 12 or a mixture according to claim 13 or claim 14, which has ferroelectric properties.
- A ferroelectric device comprising a liquid crystal compound or a mixture according to claim 20.
- 22. A liquid crystal compound according to any one of claims 1 to 12 or a mixture according to claim 13 or claim 14, which has flexo-electric properties.
- 23. A flexo-electric device comprising a liquid crystal compound or a mixture according to claim 22.

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- A liquid crystal compound according to any one of claims 1 to 12 or a mixture according to claim 13 or claim 14, which has pyro-electric properties.
 - A pyro-electric device comprising a liquid crystal compound or a mixture according to claim 24.
 - A method of preparing a liquid crystal compound of general formula (I) 26.

$$(R^1)_n$$
 $(R^3)_p$ $(R^4)_q$

(T)

where X is O, S or Se,

each R1 and R3 are independently selected from cyano, halo, optionally substituted hydrocarbyl, optionally substituted alkoxy, optionally substituted heterocyclyl, a group R¹³C(O)O- where R¹³ is optionally substituted hydrocarbyl or carboxy or a hydrocarbyl ester or amide thereof, provided that at least one or group \mathbb{R}^1 or \mathbb{R}^3 is other than cyano or halo,

each R² and R⁴ is independently selected from halo, nitro, lower alkyl optionally substituted by halo, or a group R¹⁴C(O)O- where R¹⁴ is optionally substituted hydrocarbyl,

n is 1 or 2, m is 0, 1, 2 or 3, p is 1 or 2 and q is 0 or 1, provided n + m does not exceed 4 and p + q does not exceed 2,

which method comprises either (i) reacting a compound of formula (III)

(III)

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where R², R³, R⁴, X, n, m, p and q are as defined in claim 1, and Z is either a leaving group or a group B(OH)2, with a compound of formula (TV)

 R^1-Z'

(IV)

where R1 is as defined in relation to formula (I) and Z' is a group B(OH)2 where Z is a leaving group, or a leaving group where Z is a group B(OH)2; or

(ii) reacting a compound of formula (V)



where R¹, R², R⁴, X, n, m, p and q are as defined in relation to formula (I), and Z is as defined in relation to formula (III), with a compound of formula (VI)

 R^3-Z'

(VI)

where R3 is as defined in relation to formula (I) and Z' is as defined in relation to formula (IV), or

(iii) where q is 0 and p is 1 and R³ is a carboxy group, carboxylating a compound of formula (IX)

$$(R^1)_n$$
 $(R^2)_n$
 $(R^4)_q$

(IX)

were R², R⁴, X, m,n and q are as defined in relation to formula (I), and R¹ is a group R¹ as defined in relation to formula (I) or a precursor thereof; with a carboxylating agent, and thereafter acidifying the product with an acid such as glacial acetic acid, or (IV) where q is 0, reacting a compound of formula (XIII)

(IIIX)

where R¹, R², X, n and m are as defined above, with a compound of formula (XIV)

where R^3 is a group R^3 as defined in relation to formula (I)or a precursor thereof; and thereafter, if necessary, changing any groups R^1 , R^2 R^3 or R^4 to different such groups.

27. A liquid crystal compound of general formula (I)

$$(R^{1})_{n}$$
 $(R^{3})_{p}$
 $(R^{4})_{q}$

(I)

where X is O, S or Se,

wherein one of R^1 or R^3 is cyano, and the other is optionally substituted hydrocarbyl, optionally substituted alkoxy, optionally substituted heterocyclyl, a group $R^{13}C(O)O$ -where R^{13} is optionally substituted hydrocarbyl or carboxy or a hydrocarbyl ester or amide thereof,

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each R^2 and R^4 is independently selected from halo, nitro, lower alkyl optionally substituted by halo, or a group $R^{14}C(O)O$ - where R^{14} is optionally substituted hydrocarbyl,

n is 1 or 2, m is 0, 1, 2 or 3, p is 1 or 2 and q is 0 or 1, provided n + m does not exceed 4 and p + q does not exceed 2.

A liquid crystal compound which is of general formula (IA)

where X is oxygen, sulphur or selenium, R^{1a} and R^{1b} are independently selected from hydrogen, optionally substituted cycloalkyl or optionally substituted phenyl provided that at least one group R^{1a} or R^{1b} is other than hydrogen;

one of R^{17} or R^{18} is cyano, halo, optionally substituted hydrocarbyl, optionally substituted heterocyclyl or carboxy or a hydrocarbyl ester or amide thereof, and the other is hydrogen, halo, nitro, lower alkyl optionally substituted by halo, or a group $R^{15}C(0)O$ - where R^{15} is an optionally substituted hydrocarbyl group;

 \mathbb{R}^{2n} and \mathbb{R}^{2b} are independently selected from hydrogen, halo, nitro, lower alkyl optionally substituted by halo, or a group $\mathbb{R}^{14}C(O)O$ - where \mathbb{R}^{14} is as defined above; subject to the provisos that:

(i) where X is S, R^{17} is carboxy or a hydrocarbyle ster or amide thereof, R^{18} is hydrogen, R^{2a} and R^{2b} are not both fluoro; and

(ii) the compound is other than a compound

29. A compound selected from

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2-(4-Octyloxyphenyl)-5-(4-octyloxyphenylethynyl)benzo[b]furan-6-benzoate ester
 (Compound 1)
 Ethyl-5-(4-heptylphenyl)benzo[b]furan-2-carboxylate (Compound 2)
 2-Cyano-5-(4-heptylphenyl)benzo[b]furan (Compound 3)
 (2-(4-Heptylphenyl)-5-(4-heptylphenyl)benzo[b]furan) (Compound 4)
 4-Heptylphenyl 5-(4-heptylphenyl)benzofblfuran-2-carboxylate (Compound 5)
 (2-(4-Heptylpyrimidinyl)-5-(4-heptylphenyl)benzo[b]furan) (Compound 6)
 4-Butoxyphenyl 5-(4-heptylphenyl)benzo[b]furan-2-carboxylate (Compound 7)
 4-Hexyloxyphenyl 5-(4-heptylphenyl)benzo[b]furan-2-carboxylate (Compound 8)
 4-Pentylphenyl 5-(4-heptylphenyl)benzo[b]furan-2-carboxylate (Compound No. 9)
 Methyl (2-(4-nonyloxyphenyl)-benzo[b]furan) 5-carboxylate (Compound 10)
 (S)-(+)-4-(2-Methylbutyl)phenyl 5-(4-heptylphenyl)benzo[b]furan-2-carboxylate
 (Compound 11)
 (2-(4-nonyloxyphenyl)-5-cyanobenzo[b]furan) (Compound 12)
 Methyl (2-(4-heptylphenyl)-benzo[b]furan) 5-carboxylate (Compound 13)
 (2-(4-Heptylphenyl)-5-cyanobenzo[b]furan) (Compound 14)
 (2-(4-pentylphenyl)-5-(4-heptylphenyl)benzo[b]furan) (Compound 15)
 2-Cyano-5-(4-nonyloxyphenyl)benzo[b]furan (Compound 16)
 2-(Hept-1-ynyl)-5-(4-heptylphenyl)benzo[b]furan (Compound 17)
 4-Pentylphenyl 2-(4-heptylphenyl)benzo[b]furan-5-carboxylate (Compound 189)
4-Heptylphenyl 2-(4-heptylphenyl)benzo[b]furan-5-carboxylate (Compound 19)
4-Butoxyphenyl 2-(4-heptylphenyl)benzo[b]furan-5-carboxylate (Compound 20)
4-Hexyloxyphenyl 2-(4-heptylphenyl)benzo[b]furan-5-carboxylate (Compound 21)
(S)-(+)-4-(2-Methylbutyl)phenyl 2-(4-heptylphenyl)benzo[b]furan-5-carboxylate
(Compound 22)
(S)-(+)-1-Methylheptyl 2-(4-heptylphenyl)benzo[b]furan-5-carboxylate (Compound
23)
Methyl 2-(4-heptylphenyl)benzo[b]furan-5-carboxylate (Compound 24)
2-Cyano-5-(4-propylphenyl)benzo[b]furan (Compound 25)
2-Cyano-5-(4-pentylphenyl)benzo[b]furan (Compound 26)
2-(4-Pentylphenyl)-5-cyanobenzo[b]furan Compound 27
2-Cyano-5-(4'-pentylbiphenyl)benzo[b]furan (Compound 28)
2-(4'-Pentylbiphenyl)-5-cyanobenzo[b]furan (compound 29)
2-(4-Heptylphenyl)-5-(4-pentylphenylbenzo[b]furan (Compound 30)
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2-(4-Heptylphenyl)-5-(2,3-difluoro-4-heptylphenyl)benzo[b]furan (Compound 31) 2-(2,3-difluoro-4-Heptylphenyl)-5-(4-heptylphenyl)benzo[b]furan (Compound 32) 2-(4-Heptyl)-5-(4-(4-pentylphenyl)phenyl)benzo[b]furan (Compound 33) 2-Cyano-5-(4-nonylphenyl)benzo[b]furan (Compound 34) 2-(4-Cyanophenyl)-5-(4'-pentylphenyl)benzo[b]furan (Compound 35) 2-Cyano-5-(4-octylphenyl)benzo[b]furan (Compound 36) 2-(2,3-difluoro-4-Heptylphenyl)-5-(4-heptylpyrimidinyl)benzo[b]furan (Compound 37) 6,7-Difluoro-2-(4-Heptylphenyl)-5-(4-heptylphenyl) benzo[b]furan (Compound 38) 6,7-Difluoro2-(2,3-difluoro-4-Heptylphenyl)-5-(4-heptylphenyl)benzo[b]furan (Compound 39) 2-Cyano-5-(4-hexylphenyl)benzo[b]furan (Compound 40) 2-Cyano-5-(4-pentylcyclohexyl)benzo[b]furan (Compound 41) 2-(4-Propylphenyl)-5-cyanobenzo[b]furan (Compound 42) 2-(4-Heptylphenyl)benzo[b]furan-5-carboxylic acid (Compound 43) 2-(4-heptylphenyi)benzo[b]furan-5-carboxamide (Compound 44) (Methyl 2-(4-nonyloxyphenyl)benzo[b]furan-5-carboxylate) (Compound 45) 2-(4-Nonyloxylphenyl)benzo[b]furan-5-carboxylic acid (Compound 46) 2-(4-Nonyloxylphenyl)benzo[b]furan-5-carboxamide (Compound 47) 2-Heptyl-5-(4-cyanophenyl)benzo[b]furan (Compound 48) 2-(4-pentylphenyl)-5-bromobenzo[b]furan (Compound 49) (2-(4-pentylphenyl)-5-(4'-cyanophenyl)benzo[b]furan) (Compound 50) 2-(4'-Cyanobiphenyl)-5-pentylbenzo[b]furan (Compound 51) 2-Pentyl-5-(4-(4'-cyano)biphenyl)benzo[b]furan (Compound 52) 5-(4'-Pentylcyclohexyl-4-phenyl)benzo[b]furan2-carboxylic acid (Compound 53) (5-(4'-Pentylcyclohexyl-4-phenyl)benzo[b]furan2-carboxamide) (Compound 54) 2-Cyano-5-(4'-trans-pentylcyclohexyl-4-phenyl)benzo[b]furan (Compound 55) 2-Cyanobenzo[b]furan-5-trans-(oxycarbonyl-4-pentylcyclohexane) (Compound 56) 2-(3,4-Difluorophenyl)-5-(4-heptylphenyl) benzo[b]furan (Compound 57) 6,7-Difluoro-2-(2-fluoro-(4-pentylphenyl)phenyl)-5-heptyl-benzo[b]furan (Compound 58) 6,7-Difluoro-2-(4-heptylphenyl)-5-(2,3-difluoro-4-heptylphenyl)-benzo[b]furan (Compound 59)

Ethyl-(2-heptyl)-benzo[b]furan-5-carboxylate (Compound 60)



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2-Heptyi-5-hex-2ynyl-benzo[b]furan (Compound 61) (S)-(+)-1-Methylheptyl 5-(4-heptylphenyl)benzo[b]furan-2-carboxylate (Compound 62) Ethyl 2-(4-heptylphenyl)benzo[b]furan-5-carboxylate (Compound 64) 4-Pentylphenyl 2-(4-heptylphenyl)benzo[b]furan-5-carboxylate (Compound 65) 2,5-Bis-(4-heptylphenyl)benzo[b]furan (Compound 66) 5-(4-Heptylphenyl)-2-(4-pentylphenyl)-benzo[b]furan (Compound 67) 2-(5-Heptylpyrimidin-2-yl)-5-(4-heptylphenyl)benzo[b]furan (Compound 68) 2-(3,4-Difluorophenyl)-5-(4-heptylphenyl)benzo[b]furan (Compound 69) 2-(2,3-Difluoro-4-heptylphenyl)-5-(4-heptylphenyl)benzo[b]furan (Compound 70) 2-(4-heptylphenyl)-5-(hept-1-ynylphenyl)benzo[b]furan (Compound 71) 2-(4-Heptylphenyl)-5-(4-pentylphenyl)benzo[b]furan (Compound 72) 5-(2,3-Difluoro-4-heptylphenyl)-2-(4-heptylphenyl)-benzo[b]furan (Compound 73) 2-(2,3-Difluoro-4-heptyl)-5-(5-heptylpyrimidin-2-yl)benzo[b]furan (Compound 74) 6,7-Difluoro-5-(4-heptylphenyl)-2-(4-pentylphenyl)benzo[b]furan (Compound 75) 6,7-Difluoro-2-(2,3-difluoro-4-heptylphenyl)-5-(4-heptylphenyl)benzo[b]furan (Compound 76) 2-(4-Heptylphenyl)-5-(2,3-difluoro-4-heptyl)-6,7-difluorobenzo[b]furan (Compound 77) 2-(2-Fluoro-4'-pentylbiphenyl)-6,7-difluoro-5-heptylbenzo[b]furan (Compound 78) 5-(4-Heptylphenyl)benzo[b]thiophene-2-carboxylic acid (Compound 100)

5-(4-Heptylphenyl)benzo[b]thiophene-2-carboxamide (Compound 101)

2-Cyano-5-(4-heptylphenyl)benzo[b]thiophene (Compound 102)